# *In-Situ* LCB-PP *via* High Temperature Propylene Polymerization Process (including *"Supercritical Polymerization"*)

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## List of Acronyms and Abbreviations:

| | |
|---|---|
| HMS-PP | High Melt Strength Polypropylene |
| LCB-PP | Long Chain Branched Polypropylene |
| Achieve 3825 | Linear PP resin |
| L-Catalyst | Dimethylsilylbis(2-methyl indenyl)zirconium dimethyl |
| Q catalyst | Dimethylsilylbis(2-methyl-4-phenyl indenyl)zirconium dimethyl |
| PX 514 | Supported L/MAO |
| PX 627 | Supported Q/DICOP catalyst |
| DICOP | Dimethylanilinium tetrakis(perfluorophenyl) borate |
| TEAL | Triethyl Aluminum |
| MALLS | Multi Angle Laser Light Scattering |
| $M_n$ | Number average molecular weight |
| $M_w$ | Weight average molecular weight |
| MWD | Molecular Weight Distribution |
| G | Branching Index from GPC-MALLS data |
| Tc | Crystallisation temperature |
| $\Delta H_f$ | Heat of fusion |
| MFR | Melt Flow Rate |
| Rg | Radius of Gyration |
| $\eta$ | Melt Viscosity |
| $\varepsilon$ | Shear Rate Frequency |

## Executive Summary

This report describes the effect of temperature on the ability of PX-627 catalyst to generate *in-situ* long chain branching (LCB) in a high-pressure bulk polymerization environment that extends into the supercritical regime. *In-situ* branching mechanism can be promoted if bulk propylene is polymerized at temperatures over $75^0$ C. The experiments were conducted in January 2000 as part of our effort to map temperature and dilution effects on the in-situ formation of LCB-PP. The data was generated by using a high-pressure reactor (EMR&E Laboratory, Florham Park, NJ) in the temperature range of $80\text{-}95^0$ C and pressures of 540-725 psi in the absence of hydrogen.

The key learning is that with this catalyst system the in-situ branching mechanism can be triggered if polymerization is conducted above $75^0$ C. The higher the temperature the higher the propensity for *in-situ* branching, as shown in *Figure A*. This figure was constructed using GPC-MALLS data, which provides the branching index, g. The g values less than 1.0 indicate branching and the lower the number the more extensive the branching.

Another way to fingerprint the LCB is by measuring the response of a molten polymer to elongational forces. Any positive deviation from a linear reference would indicate strain hardening that is typically associated either with MWD broadening or LCB. *Figure B* shows the extensional viscosity profile of one of the samples produced under high pressure and temperature. The extensional traces curving upward (relative to linear reference) indicate strain hardening. Since these are not broad MWD polymers, the strain hardening is clearly from the LCB.

The oscillatory shear rheological responses of the samples were also investigated to determine if they would shear-thin. There was clear evidence these materials indeed do shear-thin.

As for physical properties, the type of branching introduced by the in-situ mechanism does not alter the melting point and crystallization temperature of the LCB-PP relative to linear polymers. However, both the onset of melting and melting distribution varied depending the branching levels.

Figure A

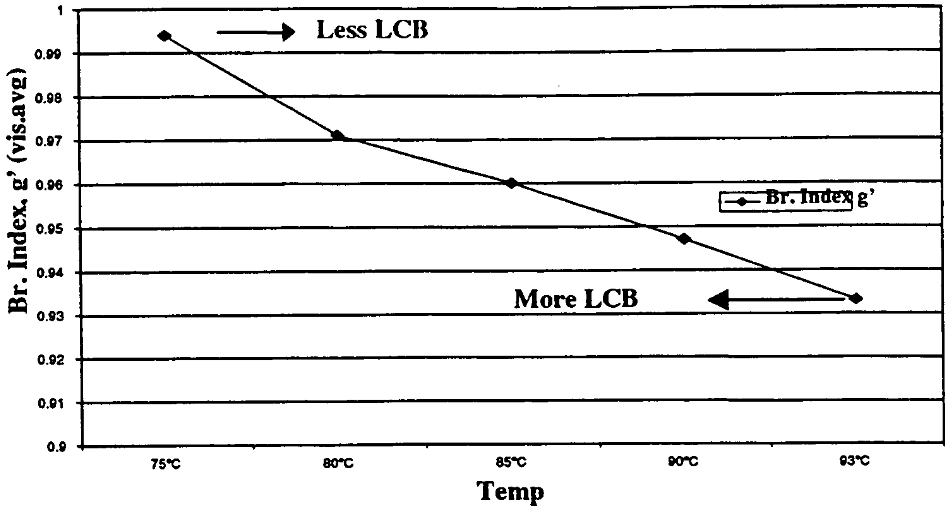
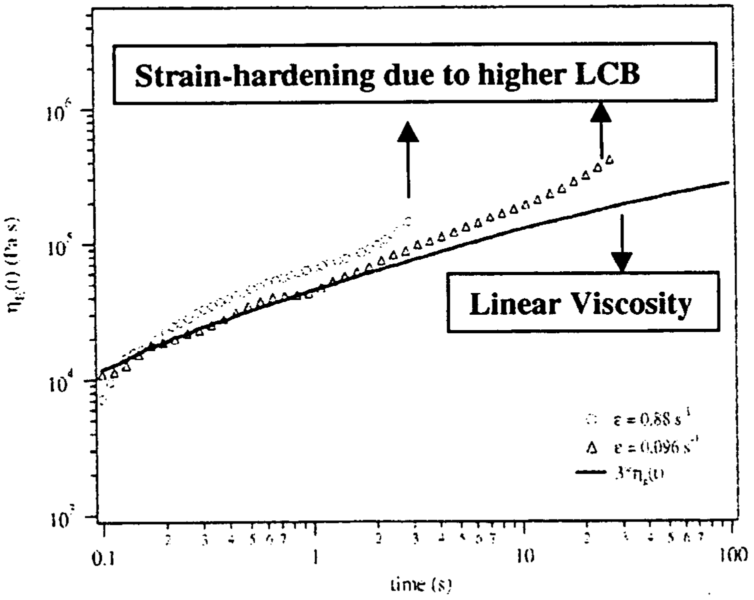


Figure: B



## Introduction:

One of the emerging frontiers in PP products is high melt strength PP. The need for HMS-PP resins stems from the fact that conventional resins have low melt strength and narrow processing windows that limit their use in thermoforming, extrusion coating, foaming, blow molding, and film applications. This limitation shows up as excess sag in sheet extrusion, rapid thinning of walls of thermoformed parts in the melt phase, low draw-down ratios in extrusion coating, poor foaming, relative weakness in large blow molded parts, and poor melt strength in films. The current global market for HMS-PP is approximately 50 million lbs;[1] the projected annual growth rate for thermoformed PP is 13%, faster than the average 8% growth rate of total PP market.[2] The materials used in the above applications are either low MFR PP or HMS-PP resins manufactured by three companies - Montell, Borealis and Chisso using post reactor modification. At present, ExxonMobil Chemical Company does not participate in many of these markets. To penetrate these sizable markets as well as expand PP market share, we have had research programs on HMS-PP for years.[3-4] One of the options we investigated involves the in-situ generation of LCB-PP.

## Background Information:

The need for HMS-PP resins has been recognized for decades and recently re-stated in a study.[2] Melt strength, which is defined as the resistance of a molten polymer to extensional flow, is a function of molecular weight and long chain branching. Improvements in melt strength and melt drawability can be achieved by introducing LCB, where the entanglement of the branched chains gives rise to higher strength and melt draw. Over the years we have identified[3-6] three different routes to LCB-PP compositions: the $\alpha,\omega$-diene, the PP macromer, and the in-situ routes. The diene approach is delicate and if not handled so can result in gels. Recent process inventions, however, have identified ways of mitigating the potential of gel formation. The macromer route generates a mixture containing unreacted, low molecular weight, PP macromers that may or may not be desirable in some applications. The *in-situ* approach, on the other hand, can produce clean HMS-PP resins without the risk of gels or large levels of residual macromers. As we reported earlier[6-7], the *in-situ* branching can be promoted if the propylene is polymerized at temperatures above $75^0$ C and under low propylene concentrations. The current PPTD commercial process involving bulk propylene polymerization at < $75^0$ C and does not produce detectable level of in-situ LCB-PPs. However, there exists another process option i.e., bulk propylene polymerization under "***supercritical***" condition.

Supercritical PP polymerization has several significant process and product advantages.

- The amount of hydrogen used is not limited by its solubility in liquid propylene, but can be mixed with propylene in any amount. This feature greatly increases the molecular weight (MW) or melt flow rate (MFR) range of the products. High MFR products can easily be produced. Bubble formation and possible circulation pump cavitation can also be avoided.

- The productivities of most polymerization processes are heat removal limited. Supercritical process increases reactor temperature from 70°C to 95°C or higher; this dramatically increases the temperature difference between the reactor and cooling jacket and improves heat transfer and reactor productivity.

- Reactor throughput can be further increased if the trend of increasing catalyst activity with rising temperature extends into supercritical range.

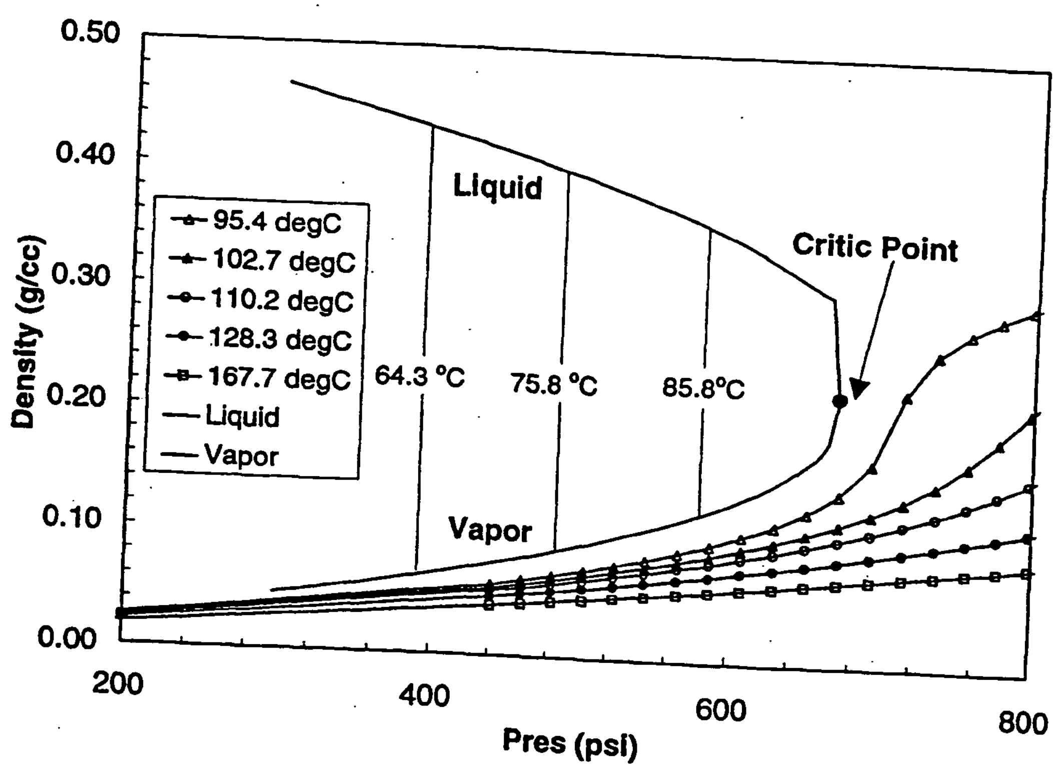
- Higher reaction rate at supercritical conditions can reduce reactor residence time and grade transition time, which makes large-scale reactors more economically attractive for producing different grades.

The key to a successful supercritical PP polymerization process relies on the availability of catalysts capable of delivering desirable product properties at high temperature. Common knowledge of polypropylene catalysts at high temperature suggest that there maybe activity loss due to catalyst deactivation, lower molecular weight due to significant chain transfer, lower crystallinity, and higher atactic fraction due to more mis-insertions.

## Propylene Phase Behavior

Before discussing supercritical propylene polymerization, it is important to understand propylene phase behavior. As reported earlier[8], *Figure 1* shows propylene density as a function of temperature and pressure around the critical point region. The reason for showing propylene density is because polymerization rate is directly proportional to monomer concentration or density. The supercritical point for propylene occurs at $T_{critical}$ = 91.4° C and at $P_{critical}$ = 660 psi pressure.

Figure 1. Propylene phase diagram using Peng-Robin Equation of State[8]



Below the critical temperature (Tc), propylene can exist as pure vapor, pure liquid or coexist as vapor and liquid. The liquid density is about 4-5 times higher than the corresponding vapor at low temperature polymerization (70°C). At normal polymerization conditions, the polymer granules are suspended in liquid propylene and vapor phase doesn't participate in the reaction. The effective monomer concentration remains constant as long as liquid propylene is present.

As temperature increases, the density of saturated vapor and liquid approach each other and become identical at the critical point. The phase boundary disappears after the critical point and only single phase exists. The monomer concentration in this region depends on the number of moles of monomer in the vessel. The effective monomer density is the average total density, which may be much lower than liquid propylene density.

## Literature Background

A recent literature search suggests that supercritical propylene polymerization is a relative new area and only a few companies are currently involved. Hoechst[9] employed supercritical technology in a second loop reactor where the copolymerization takes place. Union Carbide[10] and Mitsubishi[11] both claim to have prepared titanium based Ziegler-Natta catalysts for high temperature isotactic PP. There have been recent reports that using MAO as a cocatalyst can increase the operating temperature of Z-N PP catalysts to more than 170°C.[12] Borealis[13-14] recently demonstrated supercritical propylene homo and copolymerization with ethylene both in laboratory and pilot scale reactors.

This emerging process technology has the potential of significantly increasing productivity as well as broadening PP product window. The key to successful supercritical process relies on the availability of catalysts capable of delivering desirable product properties at high temperatures. Zhang[11] evaluated various supported catalysts under the "supercritical" propylene polymerization conditions while Brant et al[15] synthesized very low molecular weight i-PP using unsupported catalysts under similar conditions. During the early part of 2000, we investigated (*prior to Brant's work*) the effect of temperatures above $75^0$ C on the in-situ formation of LCB-PP under bulk propylene polymerizations using supported metallocene, PX 627 in a high-pressure reactor. Because the operating pressure of all lab reactors at BPC is limited to 600 psi due to safety considerations it is below the critical pressure needed for propylene (670.45 psi). Because of this limitation we used a RC-1 reaction caloriemeter (EMR&E, Florham Park) which was modified and used for all high temperature including the supercritical propylene polymerizations.

## Objective and Approach

The stated objective was to "develop catalytic /process options to produce in-situ LCB-PPs that can be implemented on current PP process platform". To do so, the following synthetic strategy was used:

- Metallocene catalyst with high comonomer incorporation ability Q-DICOP, PX 627
- High polymerization temperature (> $75^0$ C including the supercritical temperature, $91.4^0$ C) to increase the vinyl selectivity of the in-situ generated PP macromers.

Specifically, this investigation was focused on evaluating the effect of high temperature (> $75^0$ to $95^0$ C) on the formation of in-situ LCB-PP in bulk propylene polymerization.

## Experimental:

### a. Materials:

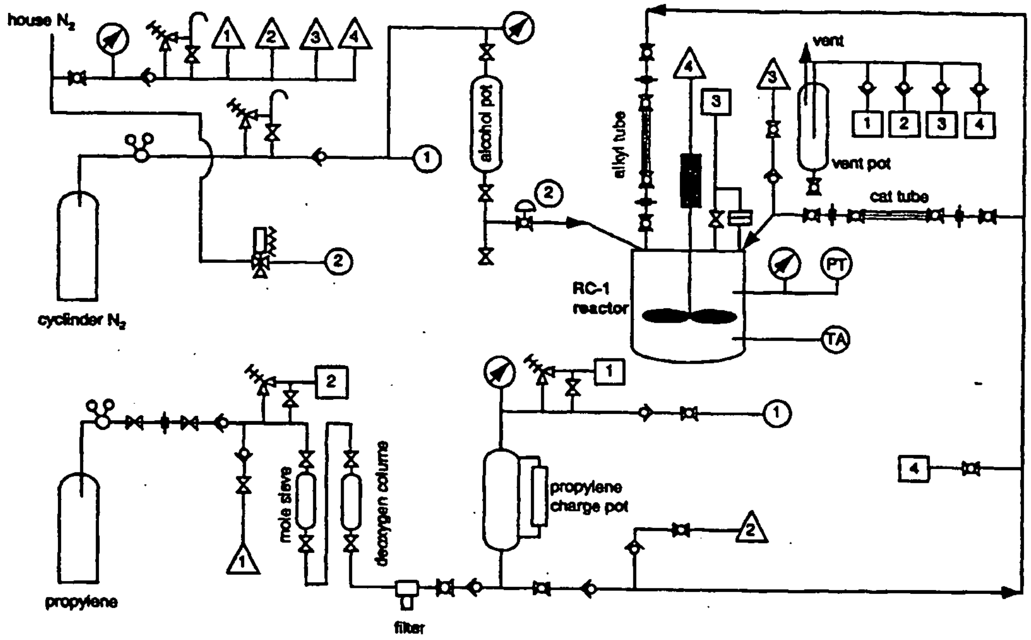
The high purity liquid $C_3^=$ monomer (99.95%) was purchased from Matheson and further purified by passing through a mole sieve column (Matheson, TX) and oxygen removal column (Labclear, CA). The desired amount of propylene was charged to the reactor from a 2L pot monitored through a calibrated Gorgensen sight-glass. The TEAL (50.8 wt% in hexane, Aldrich), and 2-Propanol (Reagent grade, Fisher Scientific) were used as purchased. J. Vizzini supplied the PX 627 catalyst formulation (10.04 wt% in white oil, NBP#: 21732-023-3) that was prepared using "Davison 952 silica, calcined at $600^0$ C".[16]

## b. Methods:

### i. High Temperature/Pressure RC-1 Reaction Calorimeter Setup:

All polymerizations were conducted in a high pressure RC-1 reaction calorimeter from Mettler. The setup and SOP of this reactor was reviewed as described previously.[8] The reactor was recertified to 80 bar (1176 psi) at a maximum operating temperature of $175^0$ C to accommodate the planned experiments. The operators (T.A. Mathew and J. Felix) were trained on the reactor by the Mettler personnel (M. Mascioli) prior to the actual run. The process flow diagram of the RC-1 reactor is shown in *Figure 2.*

Figure 2. Process Flow Diagram: RC-1 Reactor Supercritical Propylene Polymerization Setup.



### ii. High Temperature Bulk Propylene Polymerizations:

In a typical run protocol, the RC-1 reactor was cleaned, washed with hexane, checked for leaks with high pressure (700 psi) nitrogen, dried under low pressure nitrogen at $150^0$ C for 30 minutes to remove any absorbed moisture/impurities, and was then cooled to $20^0$ C keeping it under low nitrogen pressure.

The TEAL (1 ml) was injected into a specially designed reactor charge tube using a disposable syringe in a dry box. The desired amount of PX 627 catalyst in oil slurry was taken using a 16-gauge needle, weighed and injected into a catalyst-charge tube. After closing their valves, those charge tubes were installed into the reactor feed lines keeping the fittings still under nitrogen purge.

The propylene was charged into a charge pot equipped with a sight-glass, keeping it under high-pressure nitrogen. Propylene, fed in two separate portions (800 ml, 200 ml), was charged through the alkyl line and the catalyst line respectively into the reactor. After turning on the stirrer, the reactor was heated to the temperature set and was kept at that temperature for the specific time, 1 hour. The reactor was cooled down to ambient temperature as quickly as possible and the unreacted propylene was vented off. After making sure that there was no pressure inside the reactor, it was opened carefully and the reaction product was collected, dried under vacuum at 500 C for 2 hours, weighed, and used as such for further characterization.

### d. Characterization/Testing Methods:

The $^1$H-NMR was used to analyze chain end unsaturation. The molecular weight data ($M_n$, $M_w$, $M_z$) and MWD were obtained from GPC-DRI and GPC-VIS methods. Branching was measured using GPC-MALLS and are reported as "g" at each molecular weight in the GPC trace. Relating the measured g to branched structure requires the application of Zimm-Stockmayer theory, which assumes a random distribution of branch sizes for each population of branched structures (singly, doubly, triply branched, etc.) at each molecular weight.[17] The glass transition temperature (Tg) and melting point data were collected on a DuPont DSC 912 instrument with thin molded film samples, scanning at $10^0$ C/min. The melting temperatures reported were obtained from the second melt. The melt viscoelasticity data were obtained using a Rheometric Scientific RMS-800 in parallel plate oscillatory shear mode at 180° C from 0.1 to 400 rad/sec. The samples were compression molded at 180-190° C with 0.1-0.2 weight percent BHT/B225 stabilizer added to the powder samples. The complex viscosity measurements were done by subjecting these samples to a frequency sweep from 0.01 rad/s to 390 rad/s in dynamic oscillatory mode using 10% strain. The extensional viscosity data was collected by using a Rheometrics Scientific ARES at 190° C. The MFR measurements (ASTM 1238) were made using the MI instrument (BPC L121) at $190^0$ C under 2.06 kg load.

## Results and Discussion:

### 1. High Temperature/Pressure Bulk Polymerization

### a. Synthesis:

Based on previous work, the catalyst PX 627 was preferred over PX 514 because of its ability to produce relatively high vinyl terminated PP macromers and its high comonomer incorporation ability. In a typical experiment, LCB-PP was synthesized by using "*one step/ one pot*" approach. Homopolymerization of $C_3^=$ in using PX 627 catalyst in propylene slurry in the temperature range $75\text{-}95^0$ C for 60 minutes in the RC-1 high pressure reactor yielded polymers that were characterized using $^1$H NMR, DSC, MI, melt rheology, and GPC methods. The results are summarized in *Table 1.*

**Scheme 1: High temperature Propylene Polymerization**

$$C_3^= \ + \text{PX 627} \xrightarrow[80\text{-}95^0\text{ C}]{\text{RC-1 Reactor/FP Lab}} \text{LCB-PP}$$

**Table 1: High Temperature $C_3^=$ Polymerization/Characterization Data**

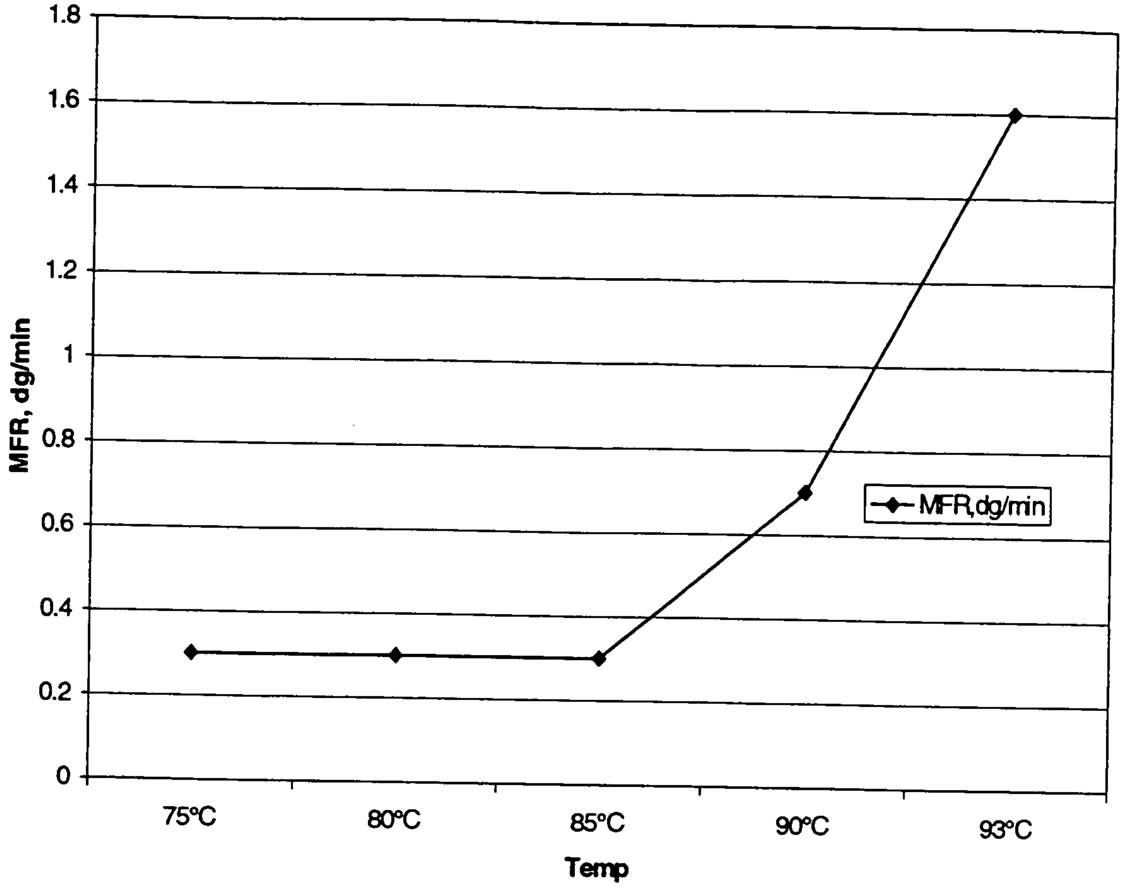
| Run# | Temp. $^0$C | Pressure psi | $^1$H NMR- Vinyl % | GPC-DRI: $M_w$, K/$M_n$, K/PD | GPC-VIS: $M_w$, K/$M_n$, K/PD | GPC-3D: g' | DSC: $T_m/T_c$, $^0$C | MF dg/m |
|---|---|---|---|---|---|---|---|---|
| 1 | 75 | 500 | 6 | 822/361/2.3 | 802/248/3.2 | 0.994 | 149/111 | 0.3 |
| 2 | 80 | 542 | 7 | 623/260/2.4 | 644/238/2.7 | 0.971 | 148/106 | 0.3 |
| 3 | 85 | 597 | 11 | 600/231/2.6 | 684/220/3.1 | 0.960 | 150/109 | 0.3 |
| 4 | 90 | 674 | 13 | 520/202/2.6 | 567/189/3.0 | 0.947 | 146/106 | 0.7 |
| 5 | 93 | 707 | 19 | 450/154/3.0 | 524/142/3.7 | 0.933 | 150/109 | 1.6 |
| 6 | 95 | 725 | 15 | 458/158/2.9 | 514/165/3.1 | 0.934 | 151/108 | 1.7 |

## b. Characterization:

The vinyl chain end selectivity was calculated from $^1$H NMR data. As expected, the MFR increased while the GPC molecular weights decreased with increasing temperatures. There were no significant differences in melting/crystallization characteristics among these products - MeltingPt/Tc: 148-151$^0$ C /106 -109$^0$ C. In general, the GPC data indicated slightly broader MWD of these products. Also, the significant difference in their $M_w$ data from two different GPC methods (*viscometry Vs conventional*) indicated qualitatively the presence of LCB structures. To confirm the above findings, both solution viscosity and the branching index, g, were deduced using GPC viscometry data. The above parameters were correlated with $M_w$. As expected, the branching indices of the above products were < 1.0, an evidence for LCB. The most compelling evidence for LCB is from GPC-MALLS data, which measures polymer coil dimensions (radius of gyration, Rg) as a function of molecular weight. By definition, the branching index, g = $(\text{Rg- branched})^2/(\text{Rg linear})^2$. The more negative the deviation from the linear control, the higher the branching. As listed in *Table 1,* the g values are < 1.0 supporting the presence of LCB structures

These results may have important commercial implications. The "*one-step/one-pot*" approach may be simple and economically more attractive to implement than other approaches such as macromer based option.

Figure 3: Effect of Temp. on MFR



## c. Effect of Polymerization Conditions on LCB

### i. Effect of Temperature:

The polymerization temperature had a major effect on the physical properties and melt behavior of the final products. As reported previously, the PP chain length decreased with increasing temperature, leading to higher MFR resins (*Figure 3*). The simultaneous increase in both vinyl selectivity and LCBs provide indirect evidence for the in-situ generation of vinyl terminated PP macromers as the key intermediate species that produce branched polymers. This observation also explains the dual role of PX-627 i.e: producing the key *"vinyl terminated macomonomers"* as building blocks and consuming them, thus generating branched-polymers.

The vinyl selectivity, as depicted in *Figure 4*, increased with higher temperatures. The % vinyl measured is the amount of macromonomer left in the polymerization pot after the polymerization is completed and does not include the amount of consumed macromonomer.

Figure 4: Effect of Temp. on Vinyl Selectivity

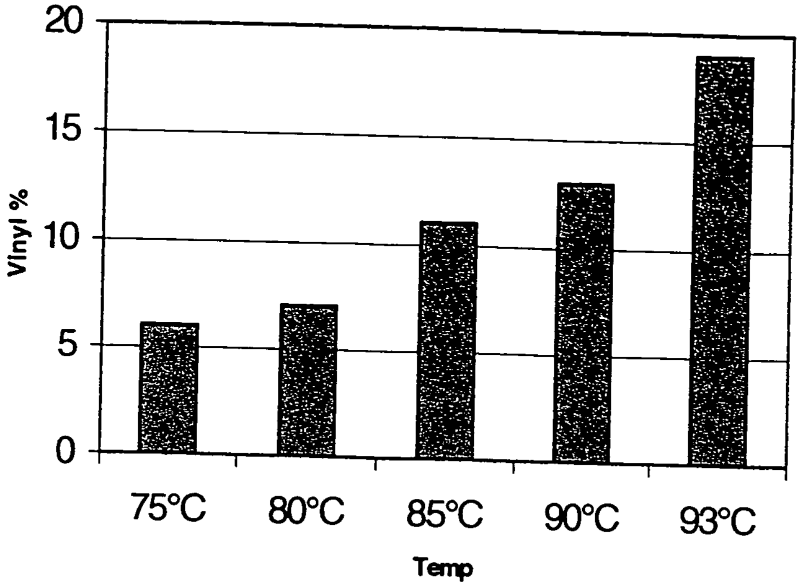


Figure 5: Effect of Temp. on in-situ Branching (100% Propylene)

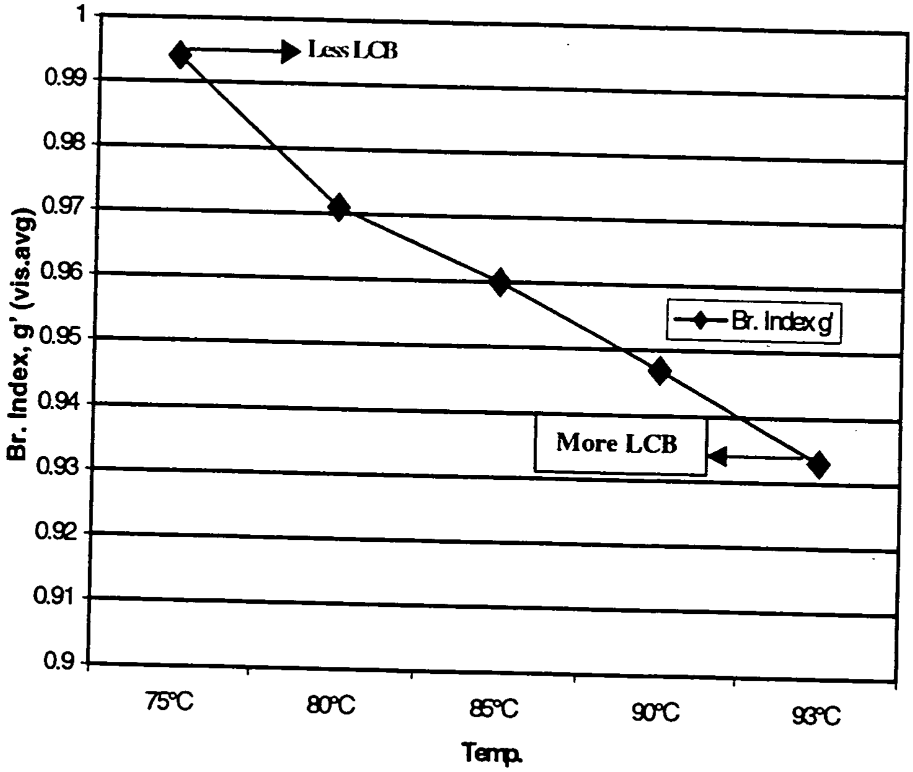


Figure 6: Effect of Temperature on LCBs (Dilute Slurry Process)

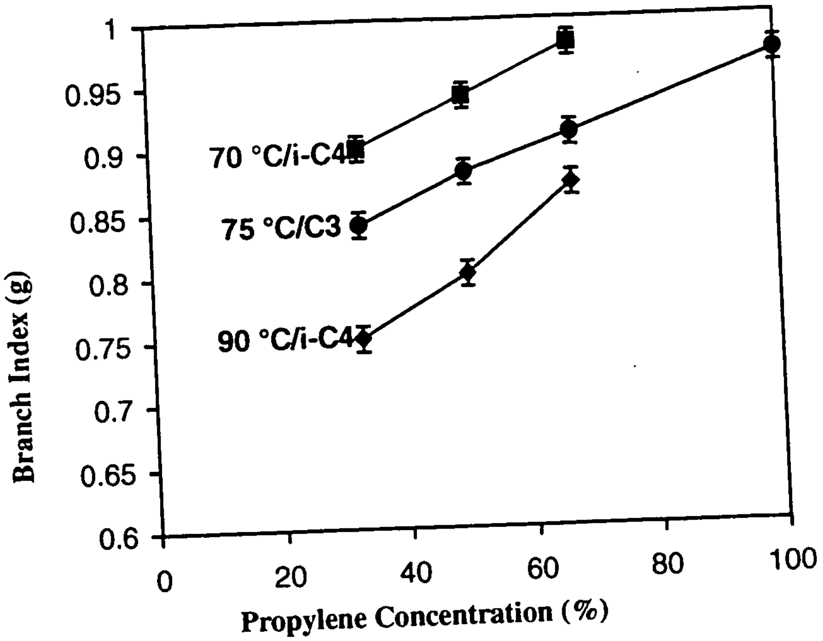
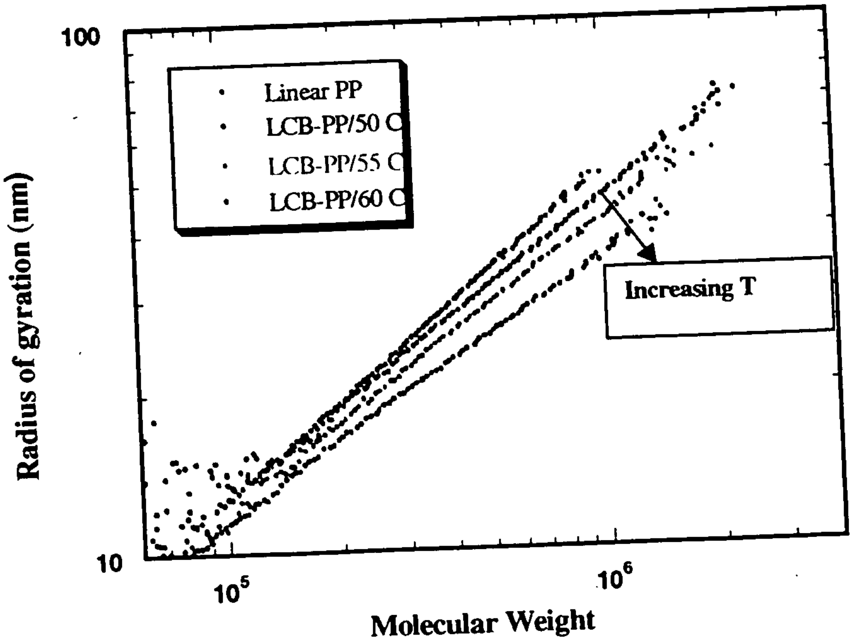


Figure 7:GPC-MALL Analysis for LCB-PP



### iv. Melt Behavior

To understand the beneficial effect of LCB on melt behavior, complex viscosity, Eta, extensional viscosity, MFR, and DSC data were collected. Analysis of the results as shown in *Table 1* indicated the following:

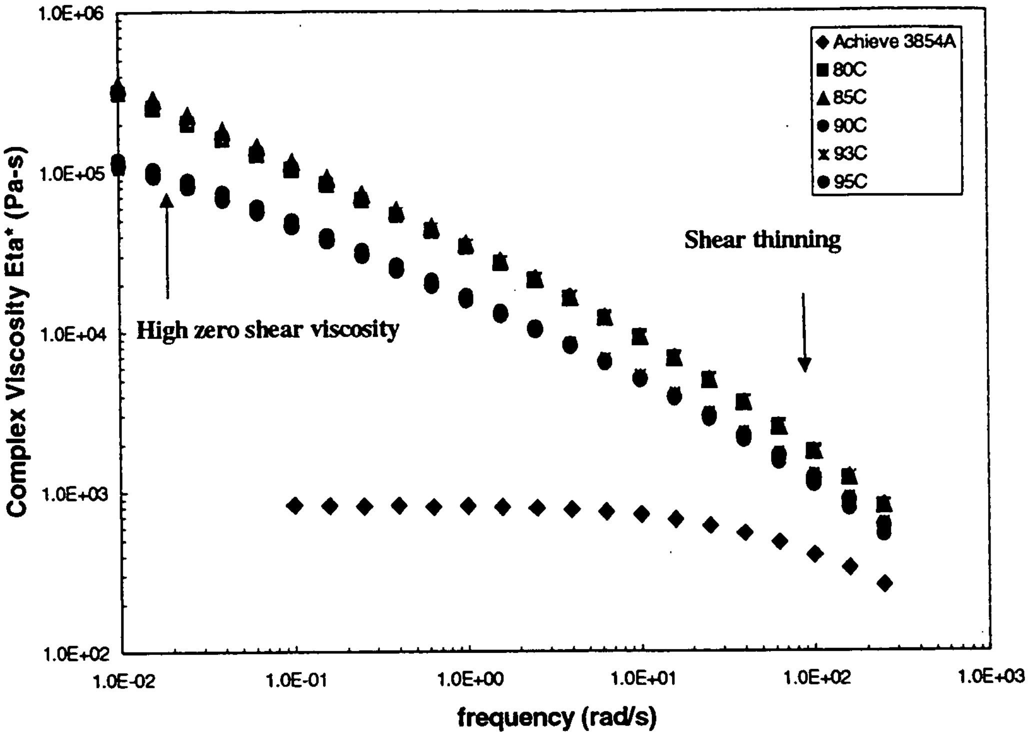
- The samples spanned a range of MFR, 0.3 to 1.7 dg/min. depending on polymerization conditions. The moderate levels of LCB in these samples do have some influence on the MFR. The higher the temperature (i.e., higher branching), the higher the MFR at similar $M_w$.

- Maintaining the high melting point is desirable for PP product performance in end-use applications. One of the major concerns for high temperature propylene polymerization is the drop in melting point due to increased mis-insertion mechanism at higher temperatures. Except in one case (*sample #4*), neither the moderate levels of LCB nor the degree of regio-defects (mis-insertion) affected the peak melting point of these samples. However, both the onset of melting and melting distribution varied depending on the branching levels. Additional NMR data is required to quantify the degree of mis-insertion in these samples to corroborate the DSC results.

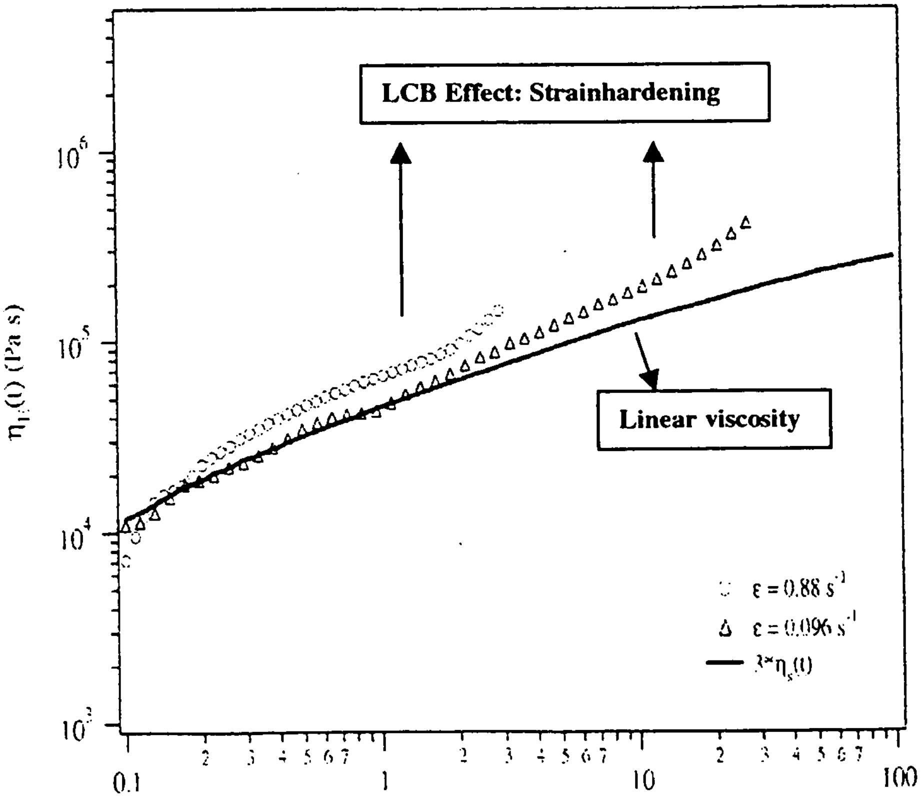
- To know the shear thinning behavior of these products, we obtained "complex viscosity, Eta, *Vs* shear rate" data under oscillatory mode. As shown in *Figure 8*, all five samples had high zero shear viscosity at low shear rate to begin with and significant drop in Eta at high shear rate. In general, shear thinning of polymers is due to both the broad MWD and LCBs. Since these products did not have broad MWD, their shear thinning behavior and hence improved processibility was mainly due to the presence of LCBs.

- One sample, *#6* exhibited higher strain-hardening in melt elongational viscosity measurements (*Figure 9*). The higher strain hardening is indicative of higher melt strength. Such high melt strength can be useful in thermoforming and other applications. Combine this with the low viscosities-cum-shear thinning of these polymers and the result is an easy-processing resin with high melt strength character.

## Figure 8: Complex Viscosity Data of in-situ LCB-PP



## Figure 9: Melt Extensional Viscosity of LCB-PP ( $95^0$ C Product)



## Summary/Conclusions:

A "one step/one pot" synthesis of *in-situ* LCB-PP was investigated. The bulk polymerization was conducted using PX 627 catalyst in the temperature range of above 75-95$^0$ C including the "*supercritical*" regime. Our results to-date indicate that it is possible to generate LCB-PP under this process conditions. The higher the polymerization temperature the higher is branchiness of the polymer.

The in-situ LCB-PP had moderate levels of LCB that increased with increasing temperatures, 75 to 95 C. The products had MFR, 0.3 to 1.7 dg/min. that increased with higher levels of branching, especially at higher temperatures and comparable $M_w$. Mostly, the presence of branching had very little effect on peak melting point. However, both the onset of melting and melting distribution varied depending the branching levels. Since there was no significant drop in melting point, these high temperature polymerization products seemed to have same degree of regio defects. These LCB-PP compositions had high zero shear viscosity and shear thinning behavior under melt. One of the above products exhibited higher strain hardening in melt elongational viscosity indicating its high melt strength. This combination of low linear viscosity-cum-shear thinning (i.e., improved processability) and high extensional viscosity (i.e., high melt strength) of these new LCB-PP compositions is somewhat unique and makes them attractive candidates for HMS-PP applications such as thermoforming, foaming, extrusion coating, blow molding, and films.

## Recommendations for Future Work

While working on the *in-situ* approach we were also investigating other options such as:

- i) PP macromer approach involving supported-metallocenes/dilute slurry process
- ii) Mixed metallocenes
- iii) Promoters such as alkenyl/alkyl silanes
- iv) Different silica supports and
- v) Combination of diene and *in-situ* mechanisms.

The major question is how to apply our learning to develop process/catalyst options to tailor make HMS-PP compositions with specific balance of properties. Further work is recommended to address the remaining issues regarding catalyst, support, modifiers, $C_3^=$ feed composition, and other process variables. Another important aspect of this work, that has progressed well to-date and will continue, is to build a strong patent portfolio.

## Acknowledgment:

This project is a result of widely cross functional team work and we would like to thank all for their valuable contribution: M. Ajinkya and John Felix/ EMR&E Labs, Florham Park, NJ for not only providing the the RC-1 Reaction Calorimeter but also setting it up for safe operability and assisting us during the polymerization runs; MCL Staff - C.J. Ruff and M. Meusz (NMR), T. Sun and D. Higgins (GPC), M.Y. Amin, J.S. Schulze, and M.K. Lyon (Rheology); J.C. Vizzini for technical discussions and providing the catalysts: PX 627; S. Zhang/Univation Technologies, BPC for technical discussion and sharing his prior experience/results of "supercritical propylene polymerization" using the RC-1 reactor; T. Hampton and L.T. Virden for literature survey; P.K. Agarwal and A.H. Dekmezian for project stewardship, and Polymer Science Management for Project support.

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